ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

LED AND VISIBLE LIGHT-INDUCED METAL FREE ATRP USING REDUCIBLE DYES IN THE PRESENCE OF AMINES

M.Sc. THESIS

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İNDİRGENEBİLİR BOYAR MADDE/AMİN SİSTEMİ İLE LED VE GÖRÜNÜR BÖLGE IŞIĞIYLA BAŞLATILMIŞ METAL İÇERİKSİZ ATRP

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ARALIK 2016

Ceren KÜTAHYA, a M.Sc. student of ITU Graduate School of Science Engineering and Technology 509141040 successfully defended the thesis entitled **"LED AND VISIBLE LIGHT-INDUCED METAL FREE ATRP USING REDUCIBLE DYES IN THE PRESENCE OF AMINES"**, which he/she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

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To my family,

FOREWORD

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ABBREVIATIONS

^{1}H-NMR	**:** Nuclear Magnetic Resonance Spectroscopy
GPC	**:** Gel Permeation Chromatography
ARGET	**:** Activators Regenerated by Electron Transfer
ATRP	**:** Atom Transfer Radical Polymerization
C/LRP	**:** Controlled/Living Radical Polymerization
EBP	**:** Ethyl 2-bromopropionate
EBI	**:** Ethyl α-bromoisobutyrate
BEB	**:** (1-Bromoethyl)benzene
E-Y	**:** Eosin Y
E-B	**:** Erythrosin B
MMA	**:** Methyl methacrylate
S	**:** Styrene
HEMA	**:** 2-Hydroxyethyl methacrylate
***t*-BA**	**:** *tert*-Butyl acrylate
NMRP	**:** Nitroxide mediated radical polymerization
PI	**:** Photoinitiator
PMDETA	**:** N, N, N', N", N"-Pentamethyldiethylenetriamine
PMMA	**:** Poly (methyl methacrylate)
RAFT	**:** Reversible Addition Fragmentation Chain Transfer
DMF	**:** N,N-Dimethylformamide
THF	**:** Tetrahydrofuran
UV	**:** Ultraviolet

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LED AND VISIBLE LIGHT-INDUCED METAL FREE ATRP USING REDUCIBLE DYES IN THE PRESENCE OF AMINES

SUMMARY

Solar energy is the basis of all changes in nature. Most typical chemical reactions such as photosynthesis is sum of a series of step reactions using solar energy. Such naturally occuring reactions give inspiration to the chemists to apply photochemical strategies on varios chemical synthesis. Photochemical synthesis holds significant advantages over the traditional routes such as thermal and spatial control and low-energy requirements. More recently, the choice of sustainable, low-energy demanding processes compare to the conventional strategies become dominant which seems to be reasonable due to the changing financial and ecological patterns of the world. The year 2015 was declared to be the "International Year of Light" by UNESCO, emphasizing the indispensable quality of light in scientific, cultural, medical and social platforms. Applications of the light energy to the polimer science spread to a broad scale resulting in an increasing number and quality of the efforts on the topic.

However, the development and utilization of environmentally friendly, reusable and low-energy using light-induced processes is still below satisfactory levels from the point of view of both academic and industrial demands. In addition, synthesis of macromolecular structures with well-defined structures and functional groups, and controlled molecular weights has become an important research field for polymer scientists. Among the controlled radical polimerization methods, atom transfer radical polymerization (ATRP) is the most-widely used method as it has high tolerance towards many functional groups present in the initiator and monomer structure and is applicable to a wide range of monomers. The major drawback associated with the ATRP process is the requirement of the low oxidation state copper halide catalytsts, which are hard to remove from the polymers obtained. The residual inorganic materials in these polymers prevent the application of these materials espacially in bioapplications. In addition, these are thermal processes and application of photochemical strategies to overcome these advantages are insufficient. Thus, additional innovative research is required due to the insufficiency of adaptation of light into the present technologies and the existence of drawbacks in the proposed strategies. In the preparation of macromolecular structures, linear polymer and network structured polymers, based on epoxy systems, synthesis deserve special attention. In this respect, photochemical methodologies are widely used as they provide low-energy requirements and simpler experimentation procedures. Recently, it has been demonstrated that some controlled polymerization techniques can be performed in the absence of inorganic catalysts by the help of light energy. Moreover, it has been also shown that the industrially applied epoxy curing can be achieved by photochemical procedures. Limited number of the existing technologies in this field proves that the topic is open to new developments and innovations.

A new photoinitiating system involving electron acceptor dyes, namely eosin Y and erythrosin B in conjunction with alkyl halides and amines for photo-induced ATRP of (meth)acrylates and vinyl monomers in the absence of inorganic catalysts is reported. The polymerizations could be efficiently activated by the photomediated redox processes producing polymers with controlled chain end functionality and narrow molecular weight distribution. The dye/amine system was shown to be efficient under various colors of LED and industrially available visible light irradiation. The livingness nature of the polymerization was proved by GC analyses and the irradiation dependency of polymerization was confirmed by light on/off experiments.

İNDİRGENEBİLİR BOYAR MADDE/AMİN SİSTEMİ İLE LED VE GÖRÜNÜR BÖLGE IŞIĞIYLA BAŞLATILMIŞ METAL İÇERİKSİZ ATRP

ÖZET

Güneş enerjisi, doğada meydana gelen tüm değişimlerin başlıca kaynağıdır. Fotosentez gibi en temel kimyasal değişimler güneş enerjisinin kullanıldığı bir seri tepkimenin sonucudur. Doğada meydana gelen bu gibi tepkimeler kimyacılar için ilham kaynağı olmuş ve fotokimyasal metotları birçok sentez tepkimesine uyarlamayı başarmışlardır. Işıkla yapılan sentezler, özellikle geleneksel yollara kıyasla, çok daha düşük enerji gerektirmesi, malzemeler üzerinde üç boyutlu kontrol sağlanmasına olanak vermesi gibi pek çok avantajları beraberinde getirmektedir. Dünyanın değişen finansal ve ekolojik koşulları göz önüne alındığında, sürdürülebilir, düşük enerji isteyen sentez yollarının eskiye kıyasla çok daha fazla tercih ediliyor olması bunu en çıplak hali ile ortaya koymaktadır. Bilindiği gibi bu bağlamda 2015 yılı UNESCO tarafından "Uluslararası Işık Yılı" olarak kabul edilmiş, ışık tabanlı teknolojilerin, bütün dünya genelinde her bilimsel platformda ve kültür, sağlık ve sosyal refahın sağlanması açısından vazgeçilmez bir unsur olduğuna vurgu yapılmıştır. Işık enerjisinin polimer bilimine olan uyarlamaları da bu anlamda çok geniş bir yelpazeye yayılmış ve gün geçtikçe bu konuda yapılan çalışmaların kalitesi ve sayısı artmıştır.

Radikalik sistemlerin bir örneği olan ve yaşayan polimerizasyon reaksiyonları olarak da bilinen, kontrollü radikal polimerizasyonu mekanizmaları, polimer zinciri molekülünün kontrollü büyümesini sağlayan ve istenilen molekül ağırlığı elde etmeye yarayan farklı polimerizasyon mekanizmalarından oluşur. Bu reaksiyonlarda, sonlanma ve başlama basamakları kontrollü bir şekilde yapılır. Bu sayede polimerin molekül ağırlığı ve polimer zincirlerinin zincir sonu grupları kontrol edilir. Geleneksel serbest radikal polimerizasyonunda polimer zincirleri ilk adımlarda hızla büyüdükleri halde, kontrollü radikal polimerizasyonda polimer zincirlerinin büyümesi doğrusal bir yol izler.

Kontrollü radikal polimerizasyonların avantajları olarak molekül ağırlığının polimer dönüşümüyle doğrusal bağıntı içinde olması, dolayısıyla istenilen molekül ağırlığının elde edilmesi, monodisperse yakın dar bir molekül ağırlığı dağılımı elde edilmesi, zincir sonunda fonksiyonel gruplara sahip polimerler elde edilmesi (telekelik polimerler), polimer moleküler mimari yapısının kontrol edilmesi (blok kopolimerler), sayılabilir.

Sonlanma ve zincir transferi reaksiyonlarının olmadığı yaşayan polimerizasyon mekanizmalarında polimer zincirinin büyüme hızı hemen hemen sabittir ve reaksiyon sonunda elde edilen polimer moleküllerinin zincir büyüklükleri birbirine çok yakındır; yani monodisperse yakın molekül ağırlığı dağılımı vardır.

Günümüzde kullanılan kontrollü radikal polimerizasyon metodlarının çoğu termal olarak başlatılmaktadır. Fotopolimerizasyon yönteminde ise bu amaç için ısı yerine ışık kullanılmaktadır. Basitçe ışıkla başlatılmış polimerizasyon reaksiyonlarına

fotopolimerizasyon denir. Genellikle mor ötesi veya görünür bölge ışık kaynakları kullanılır. Fotobaşlatıcının uygun bir dalga boyundaki ışık absorpsiyonu sonucunda oluşan primer radikaller tek fonksiyonlu monomerlerin polimerizasyonunu sağlarken çok fonksiyonlu monomerlerinde çapraz bağlı yapılara dönüştürülmesini sağlar.

Fotobaşlatıcılar, radikal oluşturma mekanizmalarına göre (birinci tip fotobaşlatıcılar) ve (ikinci tip fotobaşlatılar) fotobaşlatıcılar olmak üzere iki ayrı sınıfa ayrılır.

Birinci tip fotobaşlatıcılar, radikal vermek üzere doğrudan fotoparçalanmaya uğrayan çeşitli fonksiyonel gruplar içeren aromatik karbonil bileşiklerdir. Genellikle fotoparçalanma aromatik karbonil grubun yanındaki bağdan (α yarılması) gerçekleşir. İkinci tip fotobaşlatıcılar, (α yarılması) için gerekli olan yeterli enerjisine sahip olmadıkları için, ancak uygun hidrojen verici moleküllere enerji aktarımı veya bu moleküllerden hidrojen koparma sonucu radikalleri üretirler. En geniş kullanımı olan serbest radikal fotobaşlatıcılar, benzoin, benzil ketalleri, asetofenon türevleri, açilfosfin oksitler (birinci tip fotobaşlatıcılar) ve benzefenon, tiyokzanton, kinon/tersiyer amin kombinasyonlarıdır (ikinci tip fotobaşlatılar). UV ışığıyla fotopolimerizasyon için aktive edilen birinci tip fotobaşlatıcı bileşenleri, çok kullanışlı; fakat görünür ışık bölgesindeki kürleşmelerde yetersizlerdir. İkinci tip sistemlerde, polimerizasyonun başlaması hidrojen verici molekül üzerinde oluşan radikaller vasıtasıyla gerçekleşirken etkin olmayan ketil radikalleri birbirleriyle birleşerek ortamdan kaybolur. İkinci tip fotobaşlatıcılarda hidrojen verici moleküller olarak alkol, amin, eter ve tiyol molekülleri kullanılır. Bu moleküllerin arasında tersiyer aminler en çok tercih edilenlerdir. Ancak tersiyer aminlerin kötü kokulu, zehirli, kolay uçucu olması, göçme gibi olumsuz yönleri vardır.

Fotopolimerizasyon yönteminin kullanıldığı polimerizasyonlar daha düşük sıcaklıklarda gerçekleştirilebilmektedir. Polimerizasyonu düşük sıcaklıklarda gerçekleştirmek bir çok avantaj sağlamaktadır. Öncelikle maksimum çalışma sıcaklığı düşük olan monomerler sadece düşük sıcaklıklarda polimerleştirilebilirler, aksi halde oluşan polimerler depolimerizasyona uğrayarak tekrar monomer halini alırlar. Polimerizasyon sıcaklıklığının düşürülmesi esterleşme ve çarpaz bağlanma gibi yan reaksiyonların önlenmesini sağlarken, polimerizasyonun daha kontrollü bir şekilde yapılmasınıda sağlar. Bunlara ek olarak enzim ve protein gibi ısıya duyarlı biyoyapıların polimerizasyon işlemiyle polimerlere bağlanması gibi işlemlerde düşük sıcaklıklarda gerçekleştirilmelidir. Termal polimerizasyonla karşılaştırıldığında fotopolimerizasyon oda sıcaklığında hızlı, zamansal ve mekan kontrollü olmasından dolayı büyük avantajlara sahiptir. Fakat bu avantajların yanında fotopolimerizasyonla elde edilen polimerin molekül ağırlığı, molekül ağırlık dağılımı ve fonksiyonalitesi gibi özelliklerin kontrolü mümkün değildir. Bundan dolayıda blok ve aşı gibi kopolimerlerin sentezi fotopolimerizasyonla gerçekleşmesi kısıtlıdır. Günümüzde kullanılan iniferter, nitroksitle büyütülmüş radikal polimerizasyon, atom transfer radikal polymerizasyon (ATRP) ve tersinir katılma-ayrışma zincir transfer polimerizasyonu gibi kontrollü/yaşayan termal polimerizasyon tekniklerinin fotokimyasal başlatılmış birkaç örnekleri mevcuttur. Fotokimyasal olarak başlatılan kontrollü/yaşayan polimerizasyonlarda zincir transfer ve depolimerizasyon gibi yan reaksiyonların minimize edilmesinden dolayı daha düşük molekül ağırlık dağılımına sahip polimerler elde edilmektedir. Ayrıca uygun ışık şiddeti seçilerekte hem başlatıcı konsantrasyonu hemde polimer zincirlerinin boyu ayarlanabilir.

Bununla birlikte çevreye duyarlı, yenilenebilir, yüksek dalga boyunda ışık absorplayan ve dolayısı ile düşük enerji gerektiren yeni ışığa duyarlı sistemlerin geliştirilmesi ve kullanımı hem akademik araştırmalar, hem de ticari uygulamalar için yeterli seviyede değildir. Yine son dönemde, fonksiyonel grupları ve moleküler ağırlığı kontrol edilebilir karmaşık yapılı polimerlerin sentezi konusu, polimer bilimi ile ugraşan araştırmacılar için büyük önem taşımaktadır. Ancak, kontrollü polimerizasyon yöntemleri içinde başlatıcı ve monomer yapıları üzerindeki fonksiyonel gruplara olan toleransı ve pek çok monomere uyarlanabilmesi nedeniyle atom transfer radikal polimerizasyonu bunlar içinde en öne çıkan yöntem olmuştur. Yöntemin günümüzde ön plana çıkan en büyük zaafı ise deneyler sırasında oksijene hassas, düşük oksidasyon basamaklı bakır halojenür tuzlarına ihtiyaç duyması, fakat bu katalizörlerin deney sonucunda elde edilen polimerlerden etkin bir şekilde ayrılamamasıdır. Bu şekilde hazırlanan polimerler inorganik katı içeriği nedeniyle özellikle biyo-uygulamalar için elverişli değildir. Ayrıca süreçler termal olup, ışık enerjisinin kullanımına yönelik stratejiler bu sorunu gidermek için çok yetersiz kalmıştır. Makromoleküler yapıların, lineer polimerlerin ve epoksi bazlı çapraz bağlı polimerlerin sentezi özel önlemleri gerektirmektedir. Bu bağlamda, fotokimyasal stratejiler düşük enerji gerektirdiği ve basit deneysel süreçlerle gerçekleştirilebildiği için yaygın bir şekilde kullanılmaktadır. Yakın zamanda, bazı kontrolü kontrollü polimerizasyon tekniklerinin inorganik katalizörlere ihtiyaç duymaksızın ışık enerjisi yardımıyla gerçekleştirilebildiği gösterilmiştir. Ayrıca, endüstriyel olarak epoksi sertleştirmelerininde de fotokimyasal olarak gerçekleştirilmektedir. Bu alanda mevcut olan teknolojilerin azlığı, konu başlığının yeni gelişmelere ve keşiflere açık olduğunu ortaya koymaktadır.

Son zamanlarda, fotobaşlatılmış polimerizasyon pek çok ekonomik ve ekolojik beklentiyi biraraya getirdiği için hayli ilgi çekmektedir. Fotobaşlatılmış polimerizasyon, sahip olduğu mükemmel avantajları dolayısı ile kaplama, mürekkep, baskı levhaları, optik frekans yönlendiricileri ve mikroelektronik gibi sayısız uygulamaların temelini oluşturmaktadır. Oda sıcaklığında yüksek polimerizasyon hızı, düşük enerji tüketimi, çözücüsüz ortamada polimerizasyon, uygulanacak yüzey alanı ve uygulama süresinin kontrol edilebilmesi gibi avantajlar sağlamaktadır. Fotopolimerizasyon radikalik, katyonik ve anyonik olarak başlatılabilse de çok sayıda fotobaşlatıcının ve yüksek reaktivitedeki monomerlerin bulunulabilirliği açısından radikalik sistemlere daha fazla ilgi duyulmaktadır.

1. INTRODUCTION

In the field of polymer chemistry photoinduced chemical reactions has been widely employed. Among these reactions, light induced polymerization has many advantages in conventional radical polymerization including that it is fast, uses little energy, and easy preparation of well-defined polymer structures at low temperatures, especially at room temperature. Therefore, it has been the basis of various conventional applications in surface coatings, adhesives, microelectronics, optics and three-dimensional imaging [1, 2].

Recently, controlled/living radical polymerization (CLRP) became an established synthetic method to prepare new complex architectures of polymers with well-defined structures. The most widely studied CLRP methods are atom transfer radical polymerization (ATRP) [3, 4], reversible addition-fragmentation chain transfer polymerization (RAFT) [5, 6], nitroxide-mediated radical polymerization (NMRP) [7–9]. Among the most common controlled/living radical polymerization methods, ATRP became the most widely used strategy, due to its suitability to broad range of monomer formulations and initiators available [10]. However, the requirement of low oxidation state transition metal complexes as catalysts (i.e. CuX/L, X: halide and L: ligand) make the reaction conditions extremely sensitive to air as the corresponding metal oxides can easily be formed. Therefore, several approaches were proposed to generate the catalysts starting from their higher oxidation state analogs. Either by using organic reductants [11] or applying photochemical strategies [12–18], convenient conditions for ATRP can be provided. Among these strategies, photochemical approaches became the most-widely investigated and applied strategies as they provide temporal and spatial control over the processes [19–27]. Either by direct initiation of the Cu(II)/L at UV irradiation or indirect initiation at higher wavelengths using free radical initiators, photosensitizers, nanoparticles and porous structures in conjunction with Cu(II)/L illustrated the feasibility of conducting ATRP at ambient temperatures [28–32]. Notably, similar strategies were also applied for

copper catalyzed azide-alkyne cycloaddition reactions where the presence of CuX salts is a must [33, 34]. For example, use of polynuclear aromatic compounds (PACs) such as phenothiazine, perylene and anthracene were shown to simultaneously generate Cu(I)/L from the stable Cu(II)/L complexes, which catalyzed CuAAC for macromolecular syntheses. The mechanism considers an electron transfer from the excited state PACs (sensitizers) to Cu(II), to yield Cu(I) catalyst required [35].

Although these strategies bring enormous advantages, the necessity of inorganic catalysts in such processes could not be dealt with until recently. Recent studies showed that utilization of PACs such as phenothiazine [36–38] and perylene [39] together with alkyl halides were shown to realize ATRP even in the absence of inorganic catalyzes to produce monodisperse polymers with controlled chain-end functionalities. Previously, fluorescein was also shown to mediate ATRP in the presence of amines [40]. The mechanism involves an electron transfer from the amine to the excited state fluorescein, which reduces alkyl halides to generate radicals responsible for initiation. The reversibility of the electron transfer steps delivers the living nature of the process as well as control over chain-end functionality. In addition to these advantages, the se photo-induced metal-free ATRP systems are expected to be applicable in modification of various surfaces [41].

Eosin Y and erythrosin B are well-known electron acceptor dyes with light absorption up to around 600 nm. The halide substituents on the core chromophoric structure make them even more suitable for reduction up on photochemical excitation. Herein, we would like to present the use of two electron-acceptor dyes eosin Y and erythrosin B with electron donor amines and various alkyl halide sources to mediate metal-free photo ATRP of commercially available monomers. We performed detailed mechanistic, kinetic and spectroscopic studies and in the light of the detailed experimental evidences, we proposed a plausible polymerization mechanism.

2. THEORETICAL PART

The major concern of this thesis is to achieve controlled radical polymerization, ATRP; by photochemical means, it seemed appropriate to discuss existing controlled radical polymerization methods generally.

2.1 Controlled/Living Radical Polymerization (CLRP)

Classical radical polymerization has limitations on the basis of molecular weight and functionality control. There has been a huge effort to develop new approaches for the syntesis of polymers with narrow molecular weight distrubitions and controlled chain-end functionality [42].

In 1989, Otsu et al. introduced the idea of living polymerizations to free radical systems by the use of iniferters (initiator-transfer-agent-terminators) which can provide a degree of livingness [43]. Controlled/living radical polymerization (CLRP) allows low polydispersities (typically ranging from 1.2 to 2.0), with an almost linear increase of molar mass by time and percent conversion. CLRP techniques have been widely used due to their simplicity and applicability to a broad range of monomers, such as styrene, methyl methacrylate, n-butyl acrylate, acrylamide, acrylonitrile, and methacrylonitrile, can be polymerized in a controlled manner with various photoiniferters.

The most common methods of controlled radical polymerization are namely the atom transfer radical polymerization (ATRP) [15–17, 44–47], reversible addition-fragmentation chain transfer (RAFT) [48–51] and nitroxide-mediated radical polymerization (NMRP) [52–54], processes. Of the controlled/living radical polymerization methods, ATRP is the most widely used method because of its feasibility to a wide range of monomer formulations and initiators [10]

Polymers generated by controlled radical polymerization are used in many applications. Block copolymers for bio-applications which are mostly performed

by RAFT or ATRP, facilitate improvements in drug delivery, bio-mineralization, bio-compatibilization, and hydrogel applications. Block copolymers composed from NMRP are used in memory devices, pigment dispersion and composite manufacturing. Furthermore ATRP enables advancement in many applications which rely on tailored hydrophilicity, adhesive properties, or nanoparticle functionalization.

2.1.1 Reversible Addition/Fragmentation Chain Transfer (RAFT) Polymerization

RAFT (Reversible Addition/Fragmentation Chain Transfer) polymerization is one of the most effective methods for providing living characteristics to radical polymerization through a reversible deactivation [6, 55, 56, 58]. The main advantages of RAFT process is the ability to control the polymerization and applicability to commonly used monomers such as (meth)acrylates, (meth)acrylamides, acrylonitrile, styrenes that are suitable for radical polymerization. Another important advantage of this method over ATRP and NMRP is the tolerance of unprotected functionalities either in monomer or solvent (e.g., OH, NR_2, COOH, $CONR_2$, SO_3H) which provides a wide range of reaction conditions such as aqueous or protic media. Moreover, compatibility with polymerization processes (e.g., bulk, organic or aqueous solution, emulsion, mini-emulsion, suspension), ease of implementation and being an inexpensive technique compared to competitive ones make it one of the most important methods for controlled radical polymerization.

There is no irreversible chain transfer or termination in an ideal living polymerization; all chains are initiated at the beginning of the reaction, grow at a similar rate and survive throughout the polymerization. In RAFT polymerization; however, there are specific reagents which are capable of reversibly deactivating propagating radicals. Therefore, most of the living chains are maintained in a dormant form, and reaction conditions that support a rapid equilibrium between the active and dormant chains.

RAFT polymerization follows the mechanism as demonstrated in Figure 2.1. The RAFT agent used in the polymerization process behaves as a transfer agent. Termination is not suppressed by the RAFT process. As the thiocarbonylthio functions remain at the chain end of the growing polymer, the process features a living character and it allows the syntheses of block copolymers and telechelic polymers. For

some certain applications, the thiocarbonylthio group may need to be removed or transformed to another functional group. A number of methods to accomplish the end group removal have been devised and can be readily incorporated into polymer syntheses [59, 60].

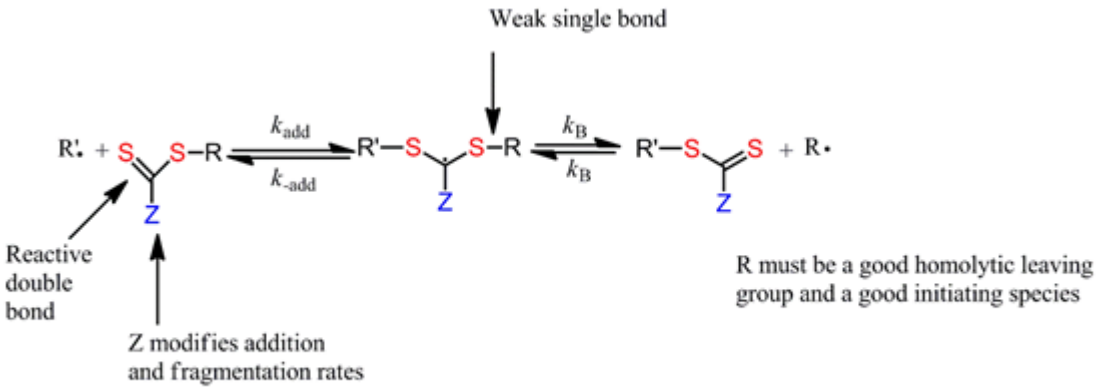


Figure 2.1: Mechanism for reversible addition-fragmentation chain transfer (RAFT).

2.1.2 Nitroxide-mediated Radical Polymerization (NMRP)

Nitroxide-mediated radical polymerization (NMRP) is one of the controlled radical polymerization methods and it is applied in wide range because the polymerizationcan be thermally initiated without an external radical source or a metal catalyst. One of the most significant advances with NMRP was the isolation of an alkoxyamine that could act as a unimolecular agent, providing both the reactive, initiating radical, and the stable, mediating nitroxide radical [61]. At first, nitroxides were used as additives to terminate polymer chains started by a radical source in a reversible manner [62]. Hawker et al. indicated an ability to adjust the molecular weight, define the end groups, and extend to block copolymers, with narrow molecular weight distributions by using 2,2,6,6 -tetramethylpiperidinyl-1-oxy (TEMPO), to trap a styrenyl radical initiated by benzoyl peroxide [8].

This mechanism considers a fast equilibrium between dormant species (TEMPO terminated chains), which are referred to as adducts and active species (i.e. growing radicals). NMRP has advantages over ATRP and RAFT on the grounds that the polymer is not contaminated with metal ions used for polymerization catalysts and avoids the use of malodorous sulfur compounds, respectively. In addition, NMRP can

be identified by use of alkoxyamine that could act as unimolecular agent, serving both as the reactive initiating radical and the stable mediating nitroxide radical [4].

The mechnanism of NMRP follows a two step mechanism. First, upon thermal treatment the initiator generates radical that adds monomer and before a propagation starts it is scavanged by TEMPO radicals. Next upon increasing the temperatures thus formed TEMPO adduct rapidly and simultaneousy forms the radicals, which provides concurrent initiation. As a result, low-dispersity polymers can be obtained.

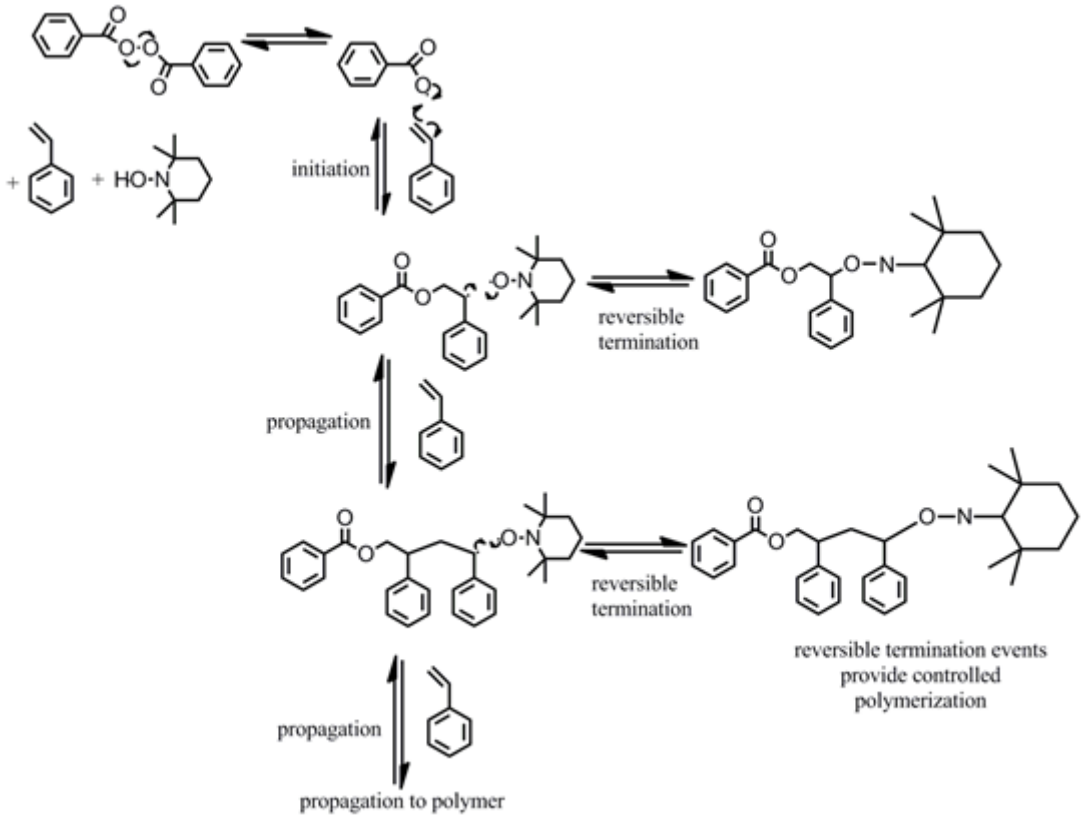


Figure 2.2: Overall mechanism for NMRP, illustrated for styrene monomer (M) polymerization initiated by benzoyl peroxide initiator (I) and mediated by TEMPO nitroxide radicals (R).

2.1.3 Atom Transfer Radical Polymerization (ATRP)

Atom transfer radical polymerization (ATRP) [4, 63–65] is the most extensively used and one of the most versatile synthetic techniques for the preparation of polymers with predetermined molecular weights, narrow molecular weight distributions (M_w/M_n, and high degrees of chain end functionalities. ATRP enables preparation of macromolecular syntheses by controlling over molecular architecture [5]. Simplicity

techniques and capability of application for wide range of monomers make this technique is the most studied and utilized of the controlled/living radical polymerization techniques [66]

Traditional ATRP requires a low-oxidation state transition metal complex (commonly CuX/L, X = Cl or Br and L = ligand) in conjunction with an appropriate alkyl halide (R-X) [67] The initiation mechanism involves a fast equilibrium of halogen abstraction/donation between CuX and R-X, where CuX_2 and R• are reversibly formed. In this fast equilibrium state, monomers can add to the alkyl radical, and the growing chains become dormant by halogen abstraction to yield CuX and Pn-X. In this equilibrium, the reverse reaction is favored and yields chains with R as the α-chain and halide as the ω-chain-end functionalities. Because of the fast initiation and the reversibility of the fast halide abstraction-donation steps, this process delivers polymers of target molecular weights with narrow molecular weight distributions [68].

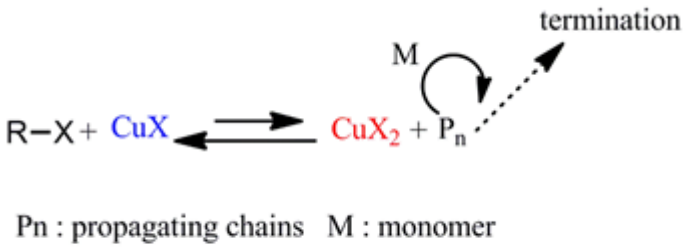


Figure 2.3: Reversibility of Atom Transfer in Conventional ATRP.

2.1.3.1 Photoinduced ATRP

Due to the high susceptibility of the catalysts to undergo oxidation, conventionally, large amounts of catalyst is used. To reduce the catalyst concentration, different approaches have been proposed. One approach considers the use of reducing agents in the polymerization media, which continuously regenerates CuX to catalyze ATRP. Other approaches are grounded on the discovery of sophisticated catalysts, which can catalyze the process even in very low concentrations.

Guan and Smart have performed to decrease the concentration of Cu catalysts in photoinduced ATRP [69] Following this study, several other approaches were reported to produce ATRP polymers using reduced amounts of inorganic catalyst.

Recently, Prof. Yagci and his group demonstrated direct photo-irradiation of Cu(II) complexes results in the formation of Cu(I) catalysts in the reaction media. The probable mechanism considers an electron transfer from the π-electrons of the ligand to the core metal to yield the Cu(I) complexes [70]. In this method, addition of methanol in the polymerization was shown to normalise the molecular weight distribution of the polymers obtained, as it further facilitates the reduction of Cu(II) species, which provides a simultaneous initiation of polymerization. The general mechanism of photo-initiated ATRP by direct irradiation is shown in Figure 2.4 [16, 17].

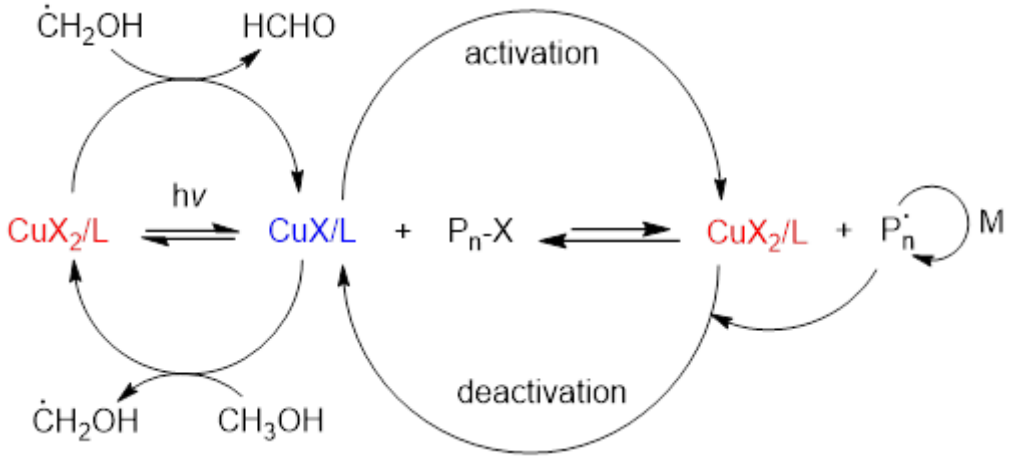


Figure 2.4: General mechanism of photo-initiated ATRP by direct irradiation using methanol.

If a free radical photoinitiator is applied and the reaction mixture is exposed to appropriate wavelength irradiation where the photoinitiator is activate, the rate of the generation of Cu(I) is t much fasterer [15, 17, 32]. General mechanism of photo-initiated ATRP by using free radical photoinitiators is demostereted in Figure 2.5.

Dimanganese decacarbonyl (Mn2(CO)10), which can abstract halides from numerous alkyl halide upon visible light irradiation can also be used in this method. Upon irradiation of the solution containing both Mn2(CO)10, RX, CuBr2/L and monomer, Cu(II)/L was reduced to Cu(I) simultaneously by the formed Mn(CO)5 species. The general mechanism of using Mn2(CO)10 in light initiated ATRP is shown below [14]. The general mechanism is shown below.

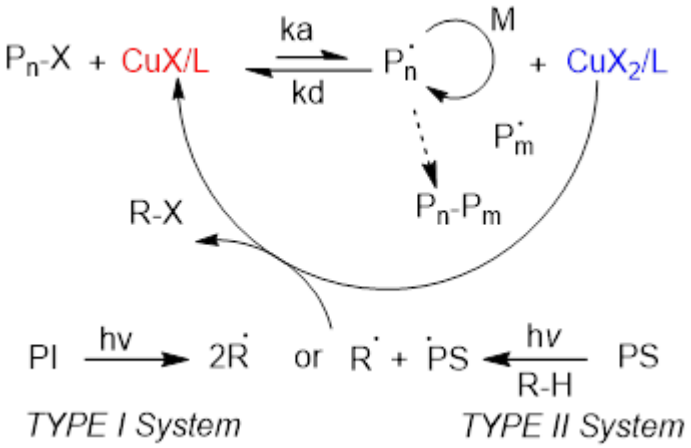


Figure 2.5: General mechanism of photo-initiated ATRP by using free radical photoinitiators.

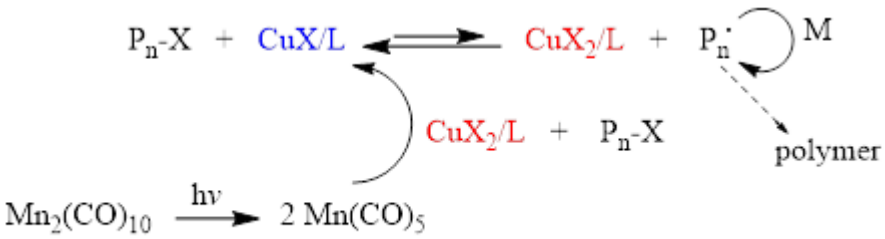


Figure 2.6: Grafting of MMA from PVC via visible light induced ATRP using $Mn_2(CO)_{10}$.

2.1.3.2 Photoinduced Metal-free ATRP

Due to the requirement of low-oxidation state transition metal complexes, strict precautions need to be taken in order to prevent the formation of metal oxides. To overcome this penalty, in situ generation of Cu(I) complexes by the reduction of the corresponding Cu(II) conjugates has been suggested. These can be performed by chemical reduction using phenols, ascorbic acid and hydrazines as reductants [11, 71] or photochemical reduction using radical photoinitiators or photosensitizers [2, 12, 15, 17].

Cu removal is especially required when polymers to be used for bioapplications, where even ppm levels of transition metal residues might be detriment. Removal of these metal complexes from the polymers is cumbersome and a number of strategies have been proposed to obtain metal-free ATRP polymers.

In 2014, Hawker and cowerkers reported a photoinduced metal-free ATRP strategy using 10-phenylphenothiazine as an organic photocatalyst [36, 72, 73]. Followingly, perylene was also used as a successful photocatalyst in conjunction with alkyl halides have been shown to realize photoinitiated CLRP of various monomers in the absence of Cu catalysts.[39] Both sensitizers generated polymers with narrow molecular weight distribution and with controlled chain-end functionalities. In a more recent study, diaryl dihydrophenazines were also shown to display favorable thermodynamic characteristics to catalyze the syntheses of polymers with tunable molecular weights and low dispersities by metal-free photoATRP.[22, 74]

Anthracene and pyrene were also studied as photosensitizers for metal free atom transfer radical polymerization of various vinyl monomers. Although anthracene was found to be more efficient in radical generation step, the detailed experiments show that anthracene/alkyl halide initiating system produces polymers via a free radical mechanism due to the transfer of the propagating sites to the labile positions on the anthracene ring. However, polymerizations using pyrene/alkyl halide system yielded polymers with narrow molecular weight distribution and controlled chain-end functionality, as confirmed by the spectroscopic analyses, and chain extension and block copolymerization experiments [75].

Previously, fluorescein was also shown to mediate ATRP in the presence of amines [76]. The mechanism involves an electron transfer from the amine to the excited state fluorescein, which reduces alkyl halides to generate radicals responsible for initiation. The reversibility of the electron transfer steps provides the living nature of the process as well as control over the chain-end functionality.

3. EXPERIMENTAL WORK

In the following all details of the materials, experimental methods and characterization techniques will be described.

3.1 Materials and Chemicals

3.1.1 Reagents

- *Methyl methacrylate* (MMA, 99%; Aldrich) : Methyl methacrylate was passed through a basic alumina column to remove the inhibitor.
- *Styrene* (St, 99%, Aldrich) : Styrene was passed through a basic alumina column to remove the inhibitor.
- *2-hydroxyethyl methacrylate* (HEMA, 99%; Aldrich) : 2-hydroxyethyl methacrylate were passed through a basic alumina column to remove the inhibitor.
- *N, N, N', N", N"-Pentamethyldiethylenetriamine* (PMDETA, 99%; Aldrich) : N, N, N', N", N"-Pentamethyldiethylenetriamine was distilled before use.
- *Ethyl α-bromoisobutyrate* (EBI, 98%, Sigma Aldrich) : Ethyl α-bromoisobutyrate was used as received.
- *Ethyl 2-bromopropionate* (EBP, 99%, Sigma Aldrich) : Ethyl 2-bromopropionate was used as received.
- *(1-bromoethyl)benzene* (BEB, 97%, Sigma Aldrich) : (1-bromoethyl)benzene was used as received.
- *Eosin Y* (C20H6Br4Na2O5, Merck, 99%) : Eosin Y was used as received.
- *Erythrosin B* (C20H6I4Na2O5, Merck, 99%) : Erythrosin B was used as received.

3.1.2 Solvents

- *N,N-dimethylformamide* (DMF, Aldrich, 99.5%) : N,N-dimethylformamide was stored over activated molecular sieves (4 Å).
- *Methanol* (99.9%; Merck) : Methanol was used as received.
- *Toluene* (Aldrich, 99.5%) : Toluene was dried with calcium chloride and distilled over sodium wire.
- *Tetrahydrofuran* (THF, Aldrich, 99.5%) : Tetrahydrofuran was dried over KOH, distilled over sodium wire, and finally distilled over sodium/benzophenone ketyl prior to use.

3.2 Equipments

3.2.1 Light Source

A Ker-Vis blue photoreactor equipped with 6 lamps (Philips TL-D 18 W) emitting light nominally at 400–500 nm was used in all polymerization experiments. The light intensity was 45 mW.cm-2 as measured by Delta Ohm model HD-9021 radiometer.

3.2.2 ^{1}H-Nuclear magnetic resonance spectroscopy (^{1}H-NMR)

^{1}H-NMR 1 pectra of 5–10 % (w/w) solutions in CDCl3 with $Si(CH_3)_4$ as an internal standard were recorded at room temperature at 250 MHz on a Bruker DPX 250 spectrometer.

3.2.3 Gel permeation chromatography (GPC)

Gel permeation chromatography (GPC) measurements were obtained from a Viscotek GPCmax Autosampler system consisting of a pump, a Viscotek UV detector and Viscotek a differential refractive index (RI) detector. Three ViscoGEL GPC columns ($G2000H_{HR}$, $G3000H_{HR}$ and $G4000H_{HR}$), (7.8 mm internal diameter, 300 mm length) were used in series. The effective molecular weight ranges were 456–42,800, 1050–107,000, and 10,200–2,890,000, respectively. THF was used as an eluent

at flow rate of 1.0 mL min^{-1} at 300^{o}C. Both detectors were calibrated with PSt standards having narrow molecular weight distribution. Data were analyzed using ViscotekOmniSEC Omni-01 software. Molecular weights of polymers were calculated with the aid of polystyrene standards.

3.3 Preparation Methods for Visible-light Induced Metal-free ATRP

MMA (2 mL, 18.6 mmol), PMDETA (19 μ L, 0.1 mmol), EBP (12.2 μ L, 0.1 mmol), DMF (1 mL) and dye (eosin Y or erythrosin B, 0.01 mmol) were put into a Schlenk tube and the reaction mixture was degassed by a freeze-pump-thaw cycle and left in vacuum. The mixture was irradiated by a Ker-Vis blue photoreactor equipped with six lamps (Philips TL-D 18 W) emitting light nominally at 400–500 nm at room temperature (or by a LED source emiting at a variety of wavelength regions). After given time, the resulted polymers were precipitated in methanol and then dried under reduced pressure. Conversion was determined gravimetrically.

4. RESULTS AND DISCUSSION

The absorption regimes of eosin Y, erythrosin B and fluorescein were tested by UV-vis spectral analysis in N,N'-dimethylformamide (DMF) (Figure 4.1). The presence of an amine (i.e., N, N, N', N", N"-pentamethyldiethylenetriamine (PMDETA)) in the solutions had a significant impact on the photophysical properties of the dyes as the five membered lactone functionality in their structures is prone to undergo a ring opening reaction at high pH levels [15]. Both eosin Y and erythrosin B display photoactivity up to 600 nm, which enables their application as photocatalysts at lower energies in comparison to fluorescein (Figure 4.1).

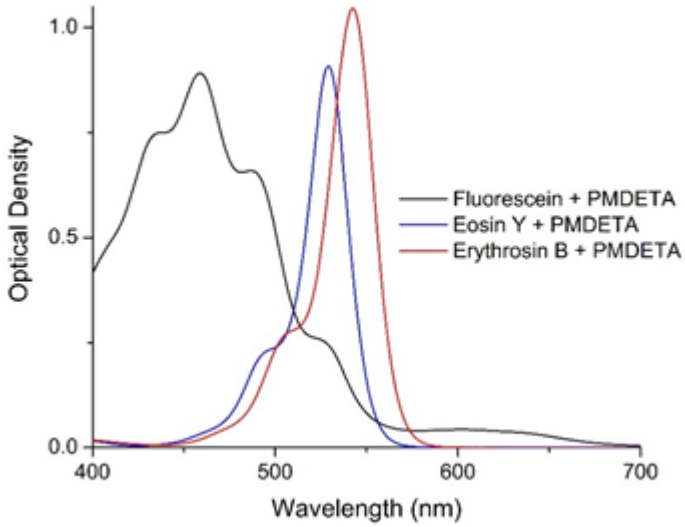


Figure 4.1: UV-vis spectra of fluorescein, eosin y and erythrosin b in the presence of PMDETA.

Steady state fluorescence studies were performed to investigate the nature of the interactions with the dyes and alkyl halides in the presence of amines. Results showed that the emission spectra of both dye/amine systems decreased with a non-linear regime upon addition of ethyl 2-bromo propionate (EBP).

Previous studies showed that structurally similar chromophores undergo a series of electron transfer reactions with the additive alkyl halide to form the corresponding

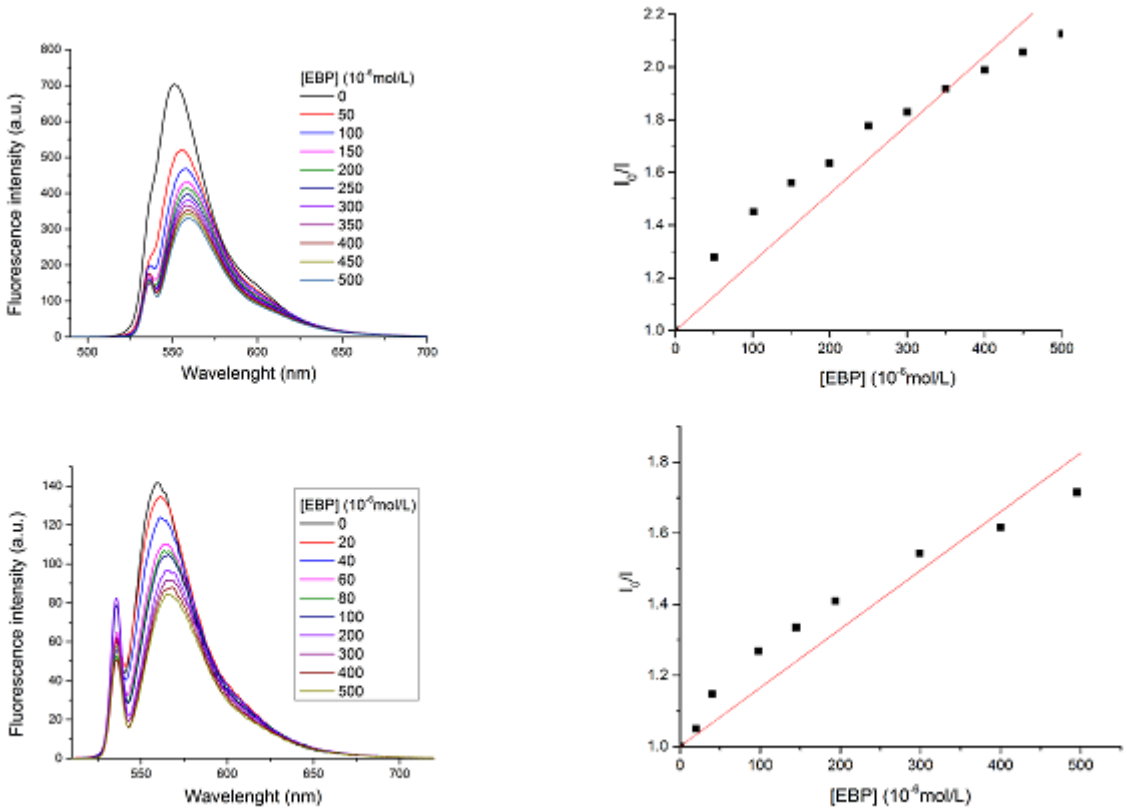


Figure 4.2: Fluorescence quenching of Erythrosin B (A) and Eosin Y (B) upon addition of ethyl 2- bromopropionate in the presence of PMDETA.

alkyl radicals through a reductive quenching mechanism upon light irradiation. These reports suggested that eosin Y and erythrosin B can be used for the photopolymerization of various monomers.

To test the ability of eosin Y and erythrosin B to mediate ATRP, methyl methacrylate (MMA) was polymerized under reduced pressure using EBP and PMDETA under visible light irradiation. For comparison, fluorescein was also used as a photosensitizer since it was previously shown to be efficient in the photo-ATRP process. The results are tabulated in Table 4.1.

The results showed that both dyes displayed a higher sensitization efficiency in comparison to fluorescein, which might be attributed to their better absorption characteristics in the irradiation region. In addition, the polymers obtained with eosin Y and erythrosin B show narrower molecular weight characteristics (runs 1-3). To gain more insight into the polymerization mechanism, similar experiments were conducted in the absence of PMDETA as the electron donor source (runs 4 and 5). However,

Table 4.1: Photoinitiated Metal Free Atom Transfer Radical Polymerization of Methyl Methacrylate Using Dyes as Photosensitizers Under Different Experimental Conditions[a]

Runs	Dye[b]	Monomer	[M]/[RX]/[PMDETA]/[Dye]	Conv.[c] [%]	M_n[d] [g·mol^{-1}]	M_w/M_n[d]
1	E-Y	MMA	200/1/1/0.1	8.7	15100	1.33
2	E-B	MMA	200/1/1/0.1	20	90000	1.20
3	F	MMA	200/1/1/0.1	9.9	17500	1.52
4	E-Y	MMA	200/1/0/0.1	–	–	–
5	E-B	MMA	200/1/0/0.1	–	–	–
6	E-Y	MMA	200/1/1/0.5	2.1	14500	1.71
7	E-B	MMA	200/1/1/0.5	-	–	–
8	F	MMA	200/1/1/0.5	22.5	11100	1.76

no polymer was attained, which proves that the presence of an electron donor source is a prerequisite for the polymerization to occur. When the concentrations of the dyes were increased, the polymerization conversions observed with both eosin Y and erythrosin B showed a dramatic decrease, but this had no effect on the conversion of the polymerization performed with fluorescein (runs 6–8). This can be accredited to the excimer (excited state dimer) formation of both eosin Y and erythrosin B, which is a wellknown phenomenon promoted by high monomer density in some specific chromophores [35]

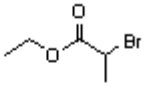
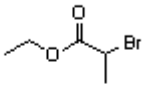
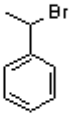
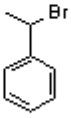
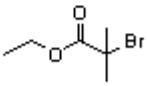
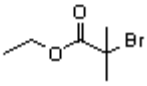
The effect of the light source on polymerization was also investigated by replacing the visible light source with an appropriate LED light. As can be seen from Table 4.2, green, white and blue LEDs lead to almost similar conversions in the polymerizations. However, higher polydispersities were observed in the polymers obtained, which might be attributed to the lower light intensities in comparison to the visible light source.

Table 4.2: Effects of light source type on photo-induced metal-free ATRP of MMA[a]

Dye[b]	LED Colour	[MMA]/[EBP]/[PMDETA]/[Dye]	Conv.[c] (%)	M_n[d] (g·mol^{-1})	M_w/M_n[d]
E-Y	Green	200/0.1/1/0.1	28	41200	1.85
E-B	Green	200/0.1/1/0.1	15.9	57600	1.42
E-Y	White	200/1/1/0.1	20.1	8700	1.48
E-B	White	200/1/1/0.1	20.0	13700	2.47
E-Y	Blue	200/1/1/0.1	20.2	31600	1.62
E-B	Blue	200/1/1/0.1	19.5	22500	1.74

The effect of the alkyl halide structure on polymerization was also investigated. Using either secondary and tertiary alkyl halides with neigh boring ester functions was shown to yield successful polymerization as well as the secondary benzyl halides, as can be seen in Table 4.3.

Table 4.3: Effects of alkyl halide structure on photo-induced metal-free ATRP of MMA[a]

Dye[b]	RX	Conv.[c] (%)	M_n[d] (g·mol^{-1})	M_w/M_n[d]
E-Y		8.7	15100	1.33
E-B		20	90000	1.2
E-Y		23	16700	2.2
E-B		11	30300	2.06
E-Y		19	24600	1.86
E-B		17	23600	1.72

The effect of the polarity of the reaction media on metalfree controlled radical polymerization was also tested. For this purpose, the typical polymerization procedures were applied with changing the polymerization solvent (Table 4.4).

Table 4.4: Effects of solvent on photo-induced metal-free ATRP of MMA using ethyl 2-bromopropionate (EBP)[a]

Dye[b]	Solvent	Conv.[c] (%)	M_n[d] (g·mol^{-1})	M_w/M_n[d]
E-Y	DMF	8.7	15100	1.33
E-B	DMF	20.0	90000	1.20
E-Y	THF	19	17100	1.41
E-B	THF	21.4	15000	1.40
E-Y	Toluene	13.6	22100	1.80
E-B	Toluene	7.5	16600	1.42

To investigate the efficiency of eosin Y in mediating the metal-free photo-ATRP of structurally different monomers, similar polymerizations were performed using styrene (S), hydroxyethyl methacrylate (HEMA) and tert-butyl acrylate (*t*-BA) (Table 4.5). All of the monomers yielded polymers with reasonable molecular weight distributions with varying conversions. The variations can be undoubtedly attributed to the propagating rate constants of the monomers.

Table 4.5: Photo-induced metal free ATRP of Various Monomers Using Eosin Y/PMDETA as Photosensitizer[a]

Monomer (M)	k_p[b] (L mol^{-1} s^{-1})	Conv.[c] (%)	M_n[d] (g mol^{-1})	M_w/M_n[d]
MMA	6.4 x 10^2	8.7	15100	1.37
S	2.4 x 10^2	2.6	4500	1.55
HEMA	2.6 x 10^3	25.1	?[e]	-
t-BA	2.8 x 10^4	42.3	47300	1.68

The light dependency of the polymerization kinetics was investigated by light on/off experiments. For this purpose, the polymerization mixtures were placed in a Schlenk tube under a nitrogen atmosphere, irradiated at $\lambda \approx$400-500 nm, and kept in dark for repeated cycles. At certain time intervals, equivalent volumes of samples were syringed out from the system and precipitated into excess methanol to gravimetrically determine the conversion and analyze the molecular weight characteristics of the polymers obtained at each step by GPC measurements. The results demonstrate the polymerization is ultimately irradiation dependent, and almost no polymerization occurred when the solutions were kept in the dark (Figure 4.3).

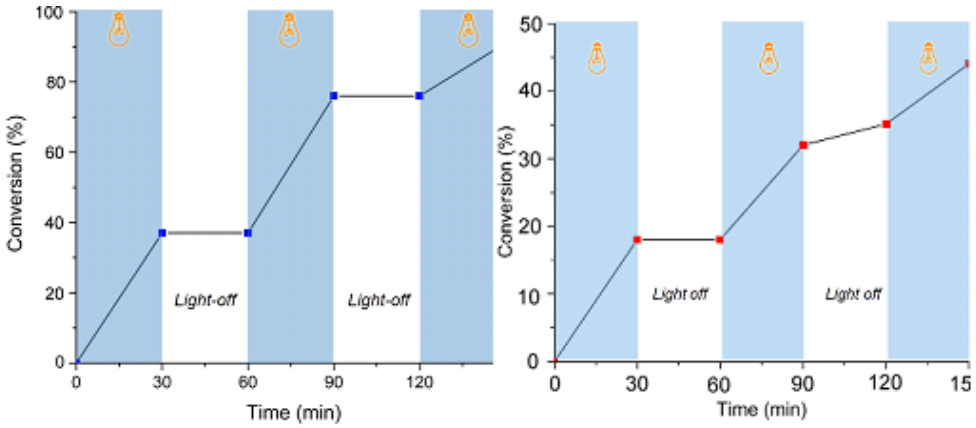


Figure 4.3: Monomer conversion (%) vs time using erythrosin B (a) and eosin Y (b) concluding the dependency of propagation on irradiation: light on (blue regions) light off (white regions).

To give further insight into the polymerization kinetics, several experiments were conducted to confirm the linear increase in the conversion during the irradiation time. A linear relationship between $ln([M]_0/[M]_t)$ and time indicated the living nature of the polymerization in the example of eosin Y (Figure 4.4).

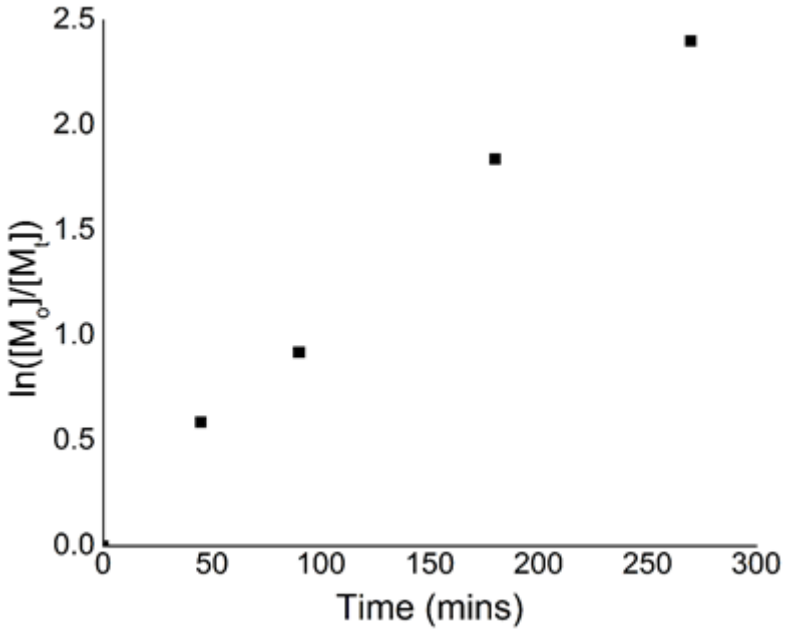


Figure 4.4: Kinetic plot of polymerization metal free ATRP using eosin Y.

In order to examine the chain-end fidelity of the polymers obtained, chain extension and block copolymerization experiments were performed. For this purpose, PMMA was used as the halide source, and identical polymerization conditions were applied as described in Table 4. GPC analyses showed that there are clear shifts to lower retention volumes, which indicated the success of the polymerizations from the chain ends of the precursor PMMA in either case (Figure 4.5).

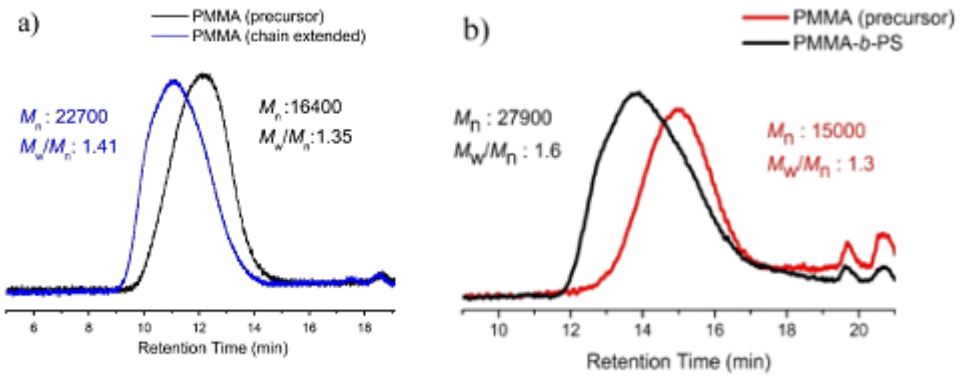


Figure 4.5: Comparison of the GPC traces of precursor PMMA with a) chain extended PMMA and b) PMMA-*b*-PS before.

In the light of these studies and the general photoexcited state behavior of the dyes, the following mechanism can be proposed for the polymerizations (Figure 4.6). The excited state dyes undergo an electron transfer with electron donor amines. The formed radical anion dyes reduce the initiator alkyl halide to yield radicals responsible for the initiation. A back electron transfer from the halide anion to the amine radical cation concludes the formation of the dormant macroalkyl halide that returns to the polymerization cycle.

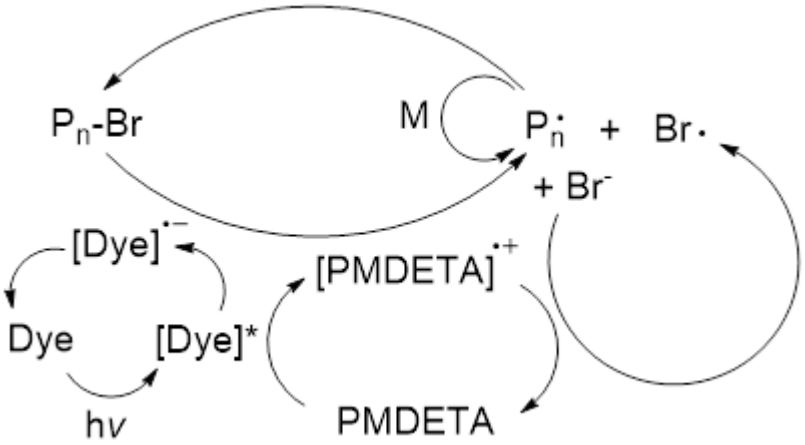


Figure 4.6: Proposed mechanism of photoinduced metal free ATRP using dye/amine initiaing system.

5. CONCLUSIONS AND RECOMMENDATIONS

In conclusion, a successful photoinduced, metal-free ATRP by using reducible dyes in the presence of amine and alkyl halides was achieved. The results of the polymerization kinetics and controlled light on/off switching polymerizations together with the chain extension and block copolymerization experiments further proved the controlled nature of the polymerization system. The possibility of using commercially available dyes and working in the visible range of the electromagnetic spectrum, specifically with newly emerging light sources like LED, contribute to the efficiency and lower cost of controlled/living radical polymerization processes.

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